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Determination of Trace Amounts of Iron(III) with 2-Dithiocarbamato Acetic Acid in Aqueous Medium by Molecular Absorption Spectrophotometry

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ABSTRACT

A simple and rapid spectrophotometric method has been developed for the determination of iron. Optimal conditions of a dark green coloured iron(III)-2-dithiocarbamato acetic acid(DTCAA) complex were determined as pH 6.6 and 400nm. The complex formed immediately and is stable for at least 3 hours. The metal to ligand ratio, linear equations for calibration, linear range were determined. The selectivity of the method was investigated. This method has been satisfactorily applied to the determination of iron in various samples such as natural water, effluent and alloys.

Keywords: Spectrophotometric, calibration, linear, selectivity, effluent and alloys.

1. INTRODUCTION

Complexes of transition metals are of fundamental chemical interest because they play a central role in a variety of industrial and biological oxidation processes[1]. Iron is one of the most important transition element in living systems[2], being vital to both plants and animals. The stunted growth of the former is well known in soils, which are either themselves deficient in iron or in which high alkalinity renders the iron too insoluble to be accessible to the plants. Iron was the first minor element to be recognized as being essential to human being and was used in the treatment of anemia. The adult human body contains about 4g of iron(i.e., ~0.005% of body weight) of which about 3g are in the form of hemoglobin. Proteins involving iron are also

present in the human body and its major function is oxygen transport and storage. In water samples, iron[3] may occur in true solution, in a colloidal state that may be peptized by organic matter, inorganic or organic iron complexes or in relatively coarse suspended particles. It may either be ferrous or ferric. Iron in water can cause staining of laundry and porcelain and a bittersweet astringent taste is detectable at levels above $1mgL^{-1}$. Therefore, the determination of iron in environmental samples has become important.

Though various spectrophotometric methods for the determination of iron have been reported[4-15] with chromogenic reagents, some with ferric and others with ferrous ion, but with these chromogenic reagents several steps are required for determination of iron and the methods are not rapid. In continuation with our development of suitable methods for the determination of metals, especially in natural samples[16-22], this paper describes a selective and improved spectrophotometric method for determining iron(III) with a new and novel chromogenic reagent, 2-dithiocarbamato acetic acid(DTCAA) in aqueous solution. The proposed method is more sensitive than the previously reported methods and has the advantages of simplicity, rapidity and stability of the colour formed.

2. EXPERIMENTAL

2.1 Instruments

Spectrophotometric measurements were carried out using Shimadzu UV-Vis spectrophotometer equipped with a quartz cell of 1.0 cm path length. A Systronics digital pH meter (model 3335) was used for the pH study.

2.2 Reagents

All of the reagents used were of analytical-reagent grade and the measurements were made at room temperature.

The ligand DTCCA was synthesized as described elsewhere[23]. The crude compound was recrystallized from ethanol-water. Analytical results: found, C-26.8, H-3.0, O-23.5, S-46.7%, calculated for C-26.5, H-2.9, O-23.5, S-47.1%. A stock solution of 1×10^{-2}M DTCAA in bidistilled water was stable for a few days and the reagent complexes in a bidentate manner.

A standard iron(III) solution (5×10^{-3} M) was prepared by dissolving 0.23g of anhydrous iron(III) chloride in 10mL of hydrochloric acid(0.1N) and diluting to 250mL with distilled water. The solution was standardised by titrimetric method using EDTA[24]. Working solutions were prepared daily by appropriate dilution of the stock solution.

Buffer solutions were prepared by appropriate mixing sodium acetate – acetic acid solutions.

2.3 Recommended procedure

In each of a set of different 25mL standard flasks, 3mL buffer solution(pH 6.6), varying volumes of 33.5-201μgmL^{-1} Fe(III) solution and 3mL of DTCAA ($1x10^{-2}$ M) were taken and the volume was made up to the mark with doubly distilled water. The absorbance was measured at 400nm against the reagent blank. The calibration curve was constructed by plotting the absorbance against the amount of iron(III). The calibration graph follows the straight line equation Y = a c + b; where c was the

concentration of the solution, Y was measured absorbance or peak height and a and b were constants.

3. RESULTS AND DISCUSSION

3.1 Absorption spectra

The absorption spectra of dark green coloured [Fe(III)-DTCAA] complex solution and the reagent blank were recorded in the wavelength region 300-800nm and shown in Fig.(1). It was observed that the complex showed the maximum absorbance at 400nm where the reagent blank had negligible absorbance. Hence, the analysis was carried out at 400nm.

3.2 Effect of pH

The experiments were conducted by mixing volumes of 1mL of 2 x 10^{-4}M Fe, 1.5mL of 2M sodium acetate solution with a pH range of 5-7. It was observed that absorbance values of the metal complex increase with increase in pH and reach a maximum at pH 6.6 and thereafter the values decrease. Since the complex formation is quantitative at pH 6.6, all the experiments were carried out at this pH only.

3.3 Effect of reagent concentration

A mixture containing 1mL of 2 x 10^{-4}M metal ion, 1.5mL of 2M sodium acetate of pH 6.6 and the reagent concentration varying between 05 - 5.0 ml of 1 x 10^{-2} DTCAA was studied. It was observed that a maximum of 3.0ml of the reagent is necessary for the quantitative complexation of iron ion and hence the same volume was used in all the experiments conducted.

3.4 Stability of the complex

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the color of the complex. It was noticed that the dark green color development was instantaneous and remained constant for more than 3 hours.

3.5 Calibration graph

Beer's law is obeyed in the concentration range 0.1–9.4μgmL^{-1} of Fe(III) as shown in Fig.(4). The molar absorptivity of the complex at 400nm and at pH 6.6 is 2.6438×10^{4}Lmol^{-1}cm^{-1}. The Sand ell's sensitivity of the method is found to be 0.0073μg/mL/cm^{2}. The standard deviation of the method for six determinations of Fe(III) was ± 0.423. The overall Physico-chemical and analytical properties of iron(III) complex with DTCAA is summarized in Table 1. The linear calibration studies are compiled in Table 2 & 3.

3.6 Reactions of DTCAA with diverse ions

We have also evaluated the effect of foreign ions(both cations and anions) on the complexation of iron by measuring the absorbance of solution containing 6.70μgmL^{-1} of iron(III) in 25mL of distilled water. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 2% in the determination of iron. The results are summed up in Table 4. The formation of the Fe(III)-DTCAA complex was not influenced by alkaline, earth alkaline ions, some transition metal ions, or other anions. The concentrations of Co^{2+}, Ni^{2+}, and Cr^{3+} in our real samples were found to be within

tolerable limits. Therefore the procedure could be applied to these samples.

3.7 Application to environmental and industrial effluents

The proposed aqueous-solution method was applied to the determination of iron in water and industrial effluents. Water sample was collected from a source that was surrounded by dyeing and food processing units, effluent samples were collected from a dyeing and tannery units. They were filtered before analysis at room temperature and transferred into a 100mL calibrated flask. A suitable aliquot of this solution was used for the iron(III) determination. The analytical results shown in Table 5 & 6 are in reasonable agreement with the standard values.

3.8 Application to Stainless steel and Chromium-nickel type steel

Known mass of the samples(~1.0g) were placed in a 100mL beaker, to it, 10mL of 20%(v/v) sulfuric acid was added and carefully covered with a watch glass until the brisk reaction subsided. The solution was heated and simmered gently after addition of 5mL of 14M HNO_3 until all carbides were decomposed. Then, 2mL solution of H_2SO_4(1:1) was added and the mixture was evaporated carefully until the dense white fumes dried off the oxides of nitrogen and then cooled at room temperature. After appropriate dilution with water, the contents of the beaker were warmed to dissolve the soluble salts. The solution was then cooled, neutralized with NH_4OH solution and filtered through a Whatman 41 filter paper into a calibrated flask of known volume. The residue was washed with a small volume of hot 1% H_2SO_4 followed by water and the volume was made up to the mark with water. The analytical results are shown in Table 7. Iron in these sample solutions could be determined rapidly and in a simplified manner.

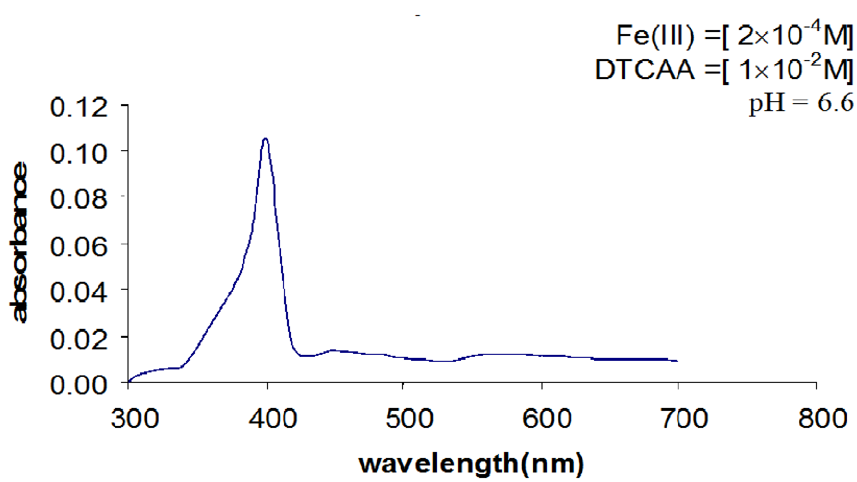

Fig.1 Absorption spectrum of Iron(III)-DTCAA complex

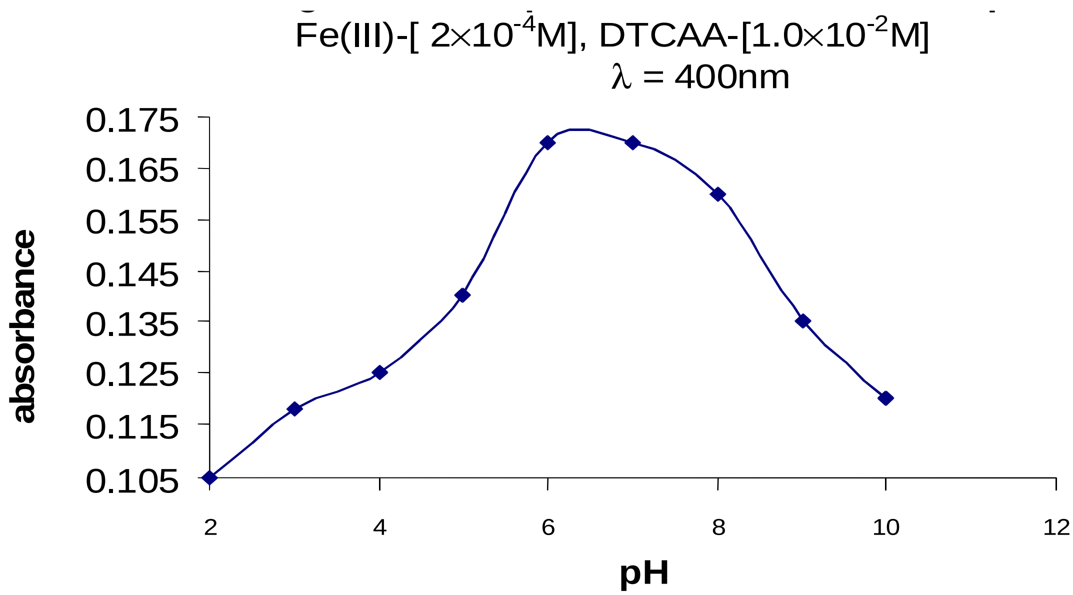

Fig. 2 Effect of pH on the Fe-DTCAA complex

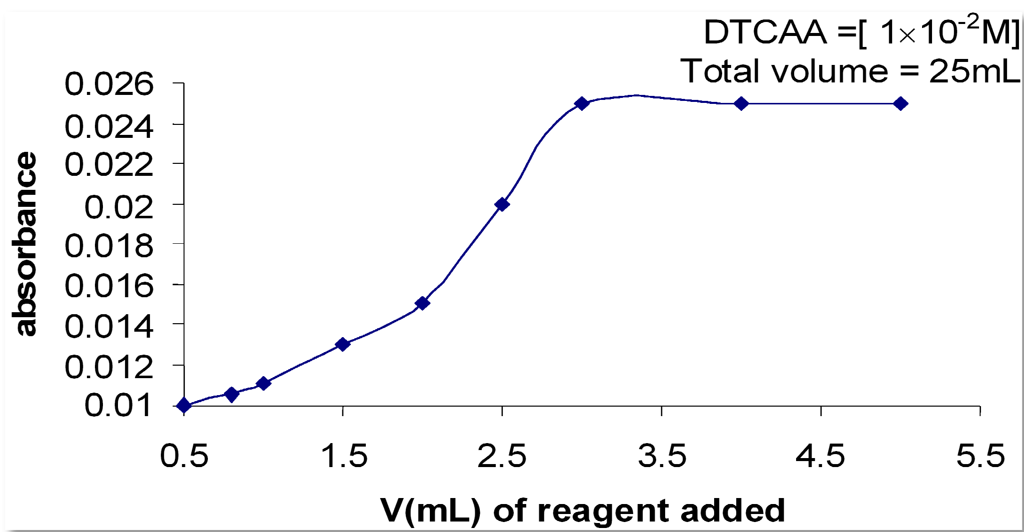

Fig. 3 Effect of amounts of reagent added

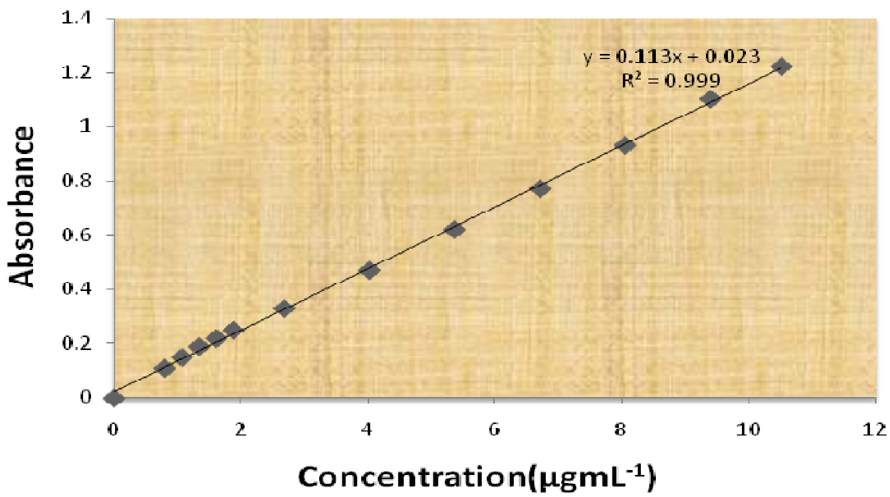

Fig. 4 Validity of Beer's Law

Table 1: Physico-chemical and analytical properties of iron(III) complex with DTCAA

S.No.	Characteristics Fe-DTCAA	
1.	λmax (nm)	400
2.	pHrange (optimum)	6.6
3.	Mole of reagent required per mole of metal ion for full colour development	20-fold
4.	Time stability of the complex (in hours)	03
5.	Beer's law validity range (µg/ml)	0 .1 - 9.4
6.	Molar absorptivity (L $mol^{-1}cm^{-1}$)	2.644 $x10^4$
7.	Sandell's sensitivity (µg of Fe(III) mL^{-1})	7.3 x 10^{-3}
8.	Composition of the complex as obtained in Job's and molar ratio methods (M:L)	1 : 2
10.	Standard deviation	0.423

Table 2 : Determination of iron(III)

	DTCAA method				Thiocyanate method		
Sl. No.	Fe(III) taken (μgmL^{-1})	Fe(III) found (μgmL^{-1})	Recovery (%)	Error (%)	Fe(III) found (μgmL^{-1})	Recovery (%)	Error (%)
1.	1.34	1.35	100.7	0.7	1.33	99.2	0.8
2.	2.68	2.70	100.7	0.7	2.66	99.2	0.8
3.	4.02	4.04	100.5	0.5	3.98	99.0	1.0
4.	5.36	5.35	99.8	0.2	5.31	99.1	0.9
5.	6.70	6.69	99.8	0.2	6.65	99.2	0.8
6.	8.04	8.05	100.1	0.1	8.00	99.5	0.5

Table 3 : Statistical Comparison

Sl. No.	Method	av. error* (%)	S.D*	C.V* (%)
1.	2-Dithiocarbamato acetic acid(DTCAA)	0.40	0.423	0.421
2.	Potassium thiocyanate	0.80	0.167	0.169

*6 replicates

Table 4: Interference studies - Amount of Iron(III) taken - 6.70μgmL^{-1}

Foreign Ions	Tolerance Limit (μgmL^{-1})
Tartarate and molybdate	650
Bromate, iodide, bicarbonate and lead(II)	620
Flouride, citrate, nitrite, ammonium(I) and silver(I)	515
Nitrate, thiosulphate, tin(II) and bismuth(II)[a]	370
Tungstate, sulphide and aluminium(III)	320
Oxalate, chloride, acetate and vanadate	215
Potassium(I), sodium(I) and magnesium(II)[a]	185
Borate, EDTA, mercury(II) and calcium(II)	150
Tetraborate, zinc(II), cobalt(II)[b] and chromium(III)[c]	90
Carbonate, cadmium(II), barium(II), strontium(II), manganese(II), nickel(II)[c] and lithium(I)	40

[a.] masked with KI(5mL, 1%w/v)
[b.] masked with NH_4OH(5mL, 1%w/v)
[c.] masked with Sodium tartarate(3mL, 1%w/v)

Table 5: Determination of Iron(III) in natural water sample

Sl. No.	Fe(III) added (μgmL^{-1})	Fe(III) found (μgmL^{-1})	recovery (%)
1.	1.34	1.39	103.7
2.	2.68	2.73	101.9
3.	4.02	3.98	99.0
4.	5.36	5.29	98.7
5.	6.70	6.60	98.5
6.	8.04	7.99	99.4

Table 6: Determination of Iron(III) in effluent (Tannery& Dyeing) sample

		Tannery		Dyeing	
Sl. No.	Fe(III) added (μgmL^{-1})	Fe(III) found (μgmL^{-1})	recovery (%)	Fe(III) found (μgmL^{-1})	recovery (%)
1.	1.34	1.38	103.0	1.39	103.7
2.	2.68	2.70	100.7	2.71	101.1
3.	4.02	4.06	101.0	4.07	101.2
4.	5.36	5.26	98.1	5.39	100.5
5.	6.70	6.63	98.9	6.65	99.2
6.	8.04	7.92	98.5	7.95	98.9

Table 7: Alloy analysis. Determination of Iron(III) in Steel Alloys

Sample Composition(%)	Sl. No.	Alloy taken (μgmL^{-1})	Fe(III) found (μgmL^{-1})	Fe(III) found (%)	av. Fe(III) (%)	S.D	C.V (%)
Stainless Steel (Cr- 11 - 13, Ni - 10, C-0.1- 0.4, Fe – 77)	1.	3.20	2.50	78.12	77.79	0.98	1.26
	2.	4.80	3.67	76.46			
	3.	6.40	4.93	77.03			
	4.	8.00	6.17	77.12			
	5.	9.60	7.59	79.06			
	6.	11.20	8.84	78.93			
Chromium-nickel type steel (Cr-16,Mn-14, Ni-1, Fe-69)	1.	3.20	2.24	70.00	68.15	3.07	4.51
	2.	4.80	3.16	65.83			
	3.	6.40	4.43	69.22			
	4.	8.00	5.45	68.12			
	5.	9.60	6.98	72.71			
	6.	11.20	8.07	63.05			

CONCLUSION

The proposed method for the spectrophotometric determination of iron(III) in water, effluents, and steel alloys were rapid, simple, selective and sensitive. In this method, organic solvents for the extraction of color derivatives have been avoided; it indicates that the present method is non-toxic and safer than those methods that use organic solvents. Statistical analysis of the results indicates that the method yield good values.

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